

# Electronic charges and electric potential at $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces studied by core-level photoemission spectroscopy

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We studied  $\text{LaAlO}_3/\text{SrTiO}_3$  interfaces for varying  $\text{LaAlO}_3$  thickness by core-level photoemission spectroscopy. In Ti  $2p$  spectra for conducting “ $n$ -type” interfaces,  $\text{Ti}^{3+}$  signals appeared, which were absent for insulating “ $p$ -type” interfaces. The  $\text{Ti}^{3+}$  signals increased with  $\text{LaAlO}_3$  thickness, but started well below the critical thickness of 4 unit cells for metallic transport. Core-level shifts with  $\text{LaAlO}_3$  thickness were much smaller than predicted by the polar catastrophe model. We attribute these observations to surface defects/adsorbates providing charges to the interface even below the critical thickness.

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Recently, heterostructures consisting of two different metal oxides have attracted considerable interest because of their fundamental interest as well as their possible device applications. At the interfaces between two band insulators,  $\text{LaAlO}_3$  and  $\text{SrTiO}_3$ , metallic conduction with high carrier mobility [1] and even superconductivity [2] have been observed. The transport at the  $\text{LaAlO}_3/\text{SrTiO}_3$  interfaces shows a remarkable termination-layer dependence [1]. That is, the  $(\text{LaO})^+/(\text{TiO}_2)^0$  interfaces exhibit metallic conductivity while the  $(\text{AlO}_2)^-/(\text{SrO})^0$  interfaces remain insulating. Moreover, the metallic transport at the  $\text{LaAlO}_3/\text{SrTiO}_3$  interfaces occurs only beyond a critical  $\text{LaAlO}_3$  layer thickness of 4-6 unit cells (uc), i.e., 1.6-2.3 nm [3, 4].

In order to interpret such properties of the interfaces, an electronic reconstruction which avoids a “polar catastrophe” has been proposed [5–8]. Because the (001) planes of  $\text{LaAlO}_3$  are polar, that is, positively charged  $(\text{LaO})^+$  and negatively charged  $(\text{AlO}_2)^-$  are alternately stacked, the electrostatic potential difference between both surfaces of the  $\text{LaAlO}_3$ (001) thin film should increase proportional to the thickness of the  $\text{LaAlO}_3$  layer. To avoid such an energetically unfavorable divergence of electrostatic potential, some charge redistribution or electronic reconstruction should take place. For the  $(\text{LaO})^+/(\text{TiO}_2)^0$  interfaces (“ $n$ -type” interfaces), the polar catastrophe can be avoided if half an electron is added to the interfacial region, resulting in the conversion of the valence of interface Ti atoms from the original  $\text{Ti}^{4+}$  to  $\text{Ti}^{4+}\text{-Ti}^{3+}$  mixed valence. For the  $(\text{AlO}_2)^-/(\text{SrO})^0$  interfaces (“ $p$ -type” interfaces), the divergence can be avoided if half an electron is removed from the interface through hole doping into the O  $2p$  band or through the formation of oxygen vacancies. On the other hand, some studies [9–11] have suggested that the interfacial conductivity originated from the formation of oxygen vacancies in the entire region of the  $\text{SrTiO}_3$ .

A cross-sectional conducting-tip atomic force microscope study of  $\text{LaAlO}_3/\text{SrTiO}_3$  interfaces [12] has revealed that the high-mobility electron gas is confined within a few nanometers when annealed in oxygen atmosphere. A recent study has shown that not only the carrier density but also the carrier mobility is a strong function of the  $\text{LaAlO}_3$  layer thickness [13]. Indeed, the generally low carrier concentration deduced from transport measurements compared to that necessary to avoid the polar catastrophe, as well as recent experimental [14] and theoretical [15, 16] studies, have pointed to major effects of carrier localization at the interfaces even above the critical  $\text{LaAlO}_3$ -layer thickness. Thus the origin of the metallic interfacial conductivity still remains highly controversial and is becoming even more non-trivial.

Photoemission spectroscopy (PES), which has been extensively used to study surface and bulk properties of solids, has been found to be a powerful technique to investigate oxide interfaces as well [17–20]. A hard x-ray PES study of the Ti core level [19] has shown that a few percent of  $\text{Ti}^{3+}$  exist within a few nanometers of the  $n$ -type  $\text{LaAlO}_3/\text{SrTiO}_3$  interface, indicating the electronic reconstruction. However, according to an x-ray photoemission (XPS) study of both  $n$ -type and  $p$ -type  $\text{LaAlO}_3/\text{SrTiO}_3$  interfaces [21], the core-level shifts were much smaller than and opposite to those predicted by the polar catastrophe model. Soft x-ray PES studies of the valence band and core levels have also been performed on the same systems by Yoshimatsu *et al* [20]. They deduced the band bending on the  $\text{SrTiO}_3$  side of the interface from the Ti  $2p$  core-level shift with varying  $\text{LaAlO}_3$  thickness, and attributed the metallic conductivity to electrons trapped by the triangular potential at the interface, although they could not detect electrons which should be doped into the Ti  $3d$  band at the  $\text{LaAlO}_3/\text{SrTiO}_3$  interface. In the present work, in order to resolve the origins of the apparently conflicting results and clarify

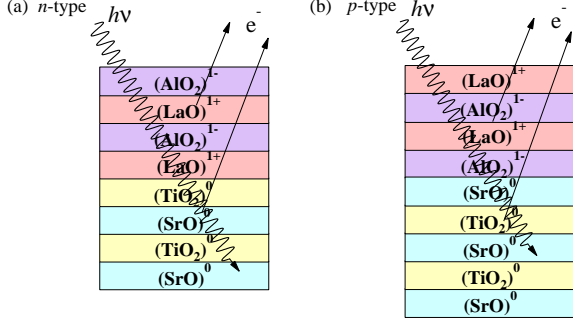


FIG. 1: (Color online) Schematic view of  $\text{LaAlO}_3$  thin films grown on  $\text{SrTiO}_3$  (001) substrates and their photoemission measurement geometry. Panels (a) and (b) represent the two types of samples assuming bulk-like charge assignments. (a)  $\text{LaAlO}_3$  is deposited on a  $\text{TiO}_2$ -terminated  $\text{SrTiO}_3$  substrate forming the “ $n$ -type” interface. (b)  $\text{LaAlO}_3$  is deposited on a  $\text{SrO}$ -terminated  $\text{SrTiO}_3$  substrate forming the “ $p$ -type” interface.

the electronic structure of the  $\text{LaAlO}_3/\text{SrTiO}_3$  interface, we have performed core-level XPS measurements with varying  $\text{LaAlO}_3$  thickness both for  $n$ -type and  $p$ -type interfaces. The results showed a systematic increase of the  $\text{Ti}^{3+}$  component in the  $\text{Ti } 2p$  core-level spectra with  $\text{LaAlO}_3$ -layer thickness only for  $n$ -type interfaces, consistent with the electronic reconstruction, whereas there was no abrupt increase at the critical  $\text{LaAlO}_3$ -layer thickness of  $\sim 4$  uc, and no clear core-level shifts for  $p$ -type interfaces. In order to interpret the experimental results, we suggest that the influence of charged surface defects has to be incorporated.

$\text{LaAlO}_3$  thin films with varying thickness from 1 to 6 uc were grown on the atomically flat,  $\text{TiO}_2$ -terminated (001) surfaces of  $\text{SrTiO}_3$  substrates using pulsed laser deposition (PLD). As schematically shown in Fig. 1(a), the  $n$ -type interface is formed when the  $\text{LaAlO}_3$  thin film is deposited onto this  $\text{TiO}_2$ -terminated surface of the  $\text{SrTiO}_3$  substrate. The  $p$ -type interface is formed when the  $\text{LaAlO}_3$  thin film is deposited onto the  $\text{SrO}$ -terminated surface of the  $\text{SrTiO}_3$  substrate [Fig. 1(b)]. Here, the  $\text{TiO}_2$ -terminated surface of the  $\text{SrTiO}_3$  (001) substrates could be converted to a  $\text{SrO}$ -terminated surface by depositing one unit cell of  $\text{SrO}$ . The heterostructures were grown at  $600^\circ\text{C}$  under an oxygen partial pressure of  $1 \times 10^{-5}$  Torr. Under this condition, the carriers are considered to be confined in the interfacial region of a few nm thickness [12]. XPS measurements were performed using a Scienta SES-100 electron-energy analyzer and a  $\text{Mg K}\alpha$  ( $h\nu = 1253.6$  eV) source. Samples were transferred from the PLD chamber to the spectrometer chamber *ex situ* and no surface treatment was performed prior to the PES measurements. All the measurements were carried out at room temperature with the total en-

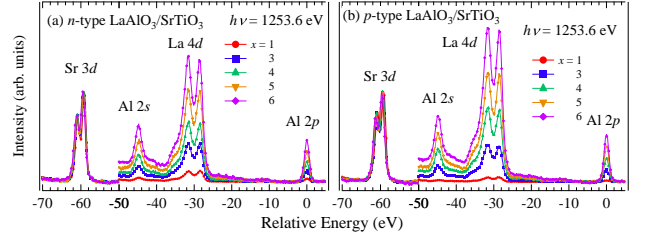


FIG. 2: (Color online) La, Al, and Sr core-level spectra of the  $\text{LaAlO}_3(x \text{ uc})/\text{SrTiO}_3$  (001) samples with varying  $\text{LaAlO}_3$ -layer thickness  $x$ . (a)  $\text{LaAlO}_3$  layer grown on the  $\text{TiO}_2$ -terminated  $\text{SrTiO}_3$  substrates forming an  $n$ -type interface. (b)  $\text{LaAlO}_3$  layer grown on the  $\text{SrO}$ -terminated  $\text{SrTiO}_3$  substrates forming a  $p$ -type interface. All the spectra have been normalized to the area of the Sr  $3d$  core-level spectrum and the Sr  $3d$  core-level peak positions have been aligned.

ergy resolution of about 800 meV.

Figure 2 shows the La, Al, and Sr core-level spectra of the  $\text{LaAlO}_3$  thin films grown on the termination-layer-controlled  $\text{SrTiO}_3$  substrates as described above. Because of unavoidable charging effects of the entire sample and resultant uncertainties in the absolute binding energies, the spectra have been aligned to the peak position of the Sr  $3d$  core level. All the spectra have been normalized to the intensity of the Sr  $3d$  core level. With increasing  $\text{LaAlO}_3$  thickness, the intensity of the La and Al core level systematically increases.

Figure 3 shows the  $\text{Ti } 2p$  core-level spectra of the same samples. The spectra have been aligned to the  $\text{Ti } 2p_{3/2}$  peak position and normalized to its peak height. For the  $\text{LaAlO}_3$  thin films grown on  $\text{TiO}_2$ -terminated  $\text{SrTiO}_3$  substrates forming  $n$ -type interfaces [Fig. 3(a)], one can see an additional feature which can be assigned to  $\text{Ti}^{3+}$  [22] on the lower binding-energy side of the  $\text{Ti } 2p_{3/2}$  peak and grows with the  $\text{LaAlO}_3$ -layer thickness. In order to evaluate the amount of the  $\text{Ti}^{3+}$  signal, we have subtracted the spectrum of  $\text{SrTiO}_3$  and evaluated the area of the  $\text{Ti}^{3+}$  components by a standard line-shape fitting. Figure 3(c) shows the resulting  $\text{Ti}^{3+}$  intensity as a function of the  $\text{LaAlO}_3$ -layer thickness. Already for thickness as small as 1 uc, a weak  $\text{Ti}^{3+}$  component ( $\sim 1\%$  of the  $\text{Ti}^{4+}$  peak) appeared and grew to  $\sim 3\%$  for thicknesses greater than 3 uc. Combining this  $\text{Ti}^{3+}/\text{Ti}^{4+}$  intensity ratio and the mean-free path of photoelectrons of  $\sim 2$  nm ( $\sim 5$  uc), the total amount of  $\text{Ti}^{3+}$  per 2D unit cells is estimated to be at least 0.10 - 0.15 [23], and the 2D carrier density is estimated to be at least  $\sim 10^{14} \text{ cm}^{-2}$ , significantly larger than  $\sim 2 \times 10^{13} \text{ cm}^{-2}$  [4] estimated from the transport measurements. This indicates that a considerable portion of electrons at the  $n$ -type interfaces are localized, and are probably responsible for the magnetism of the interfaces [14].

Another point to note is that, while the transport data show an abrupt increase of conductivity above the critical  $\text{LaAlO}_3$ -layer thickness of 4 uc, the  $\text{Ti}^{3+}$  intensity

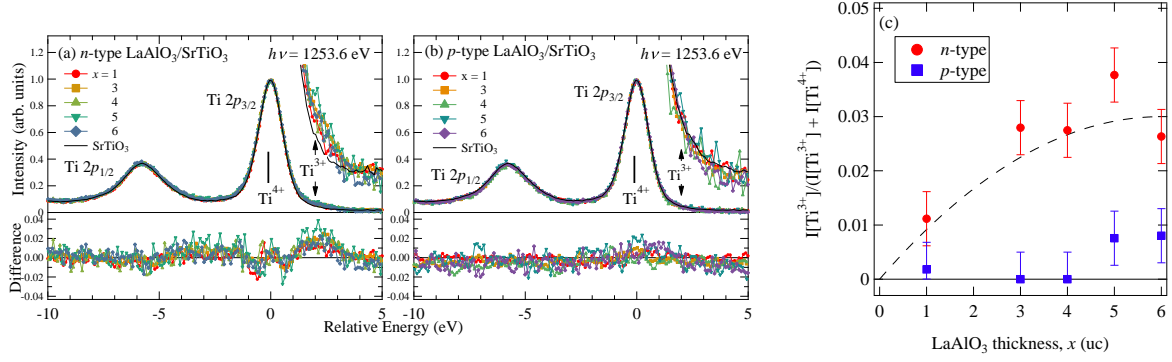


FIG. 3: (Color online) Ti 2p core-level spectra of LaAlO<sub>3</sub>( $x$  uc)/SrTiO<sub>3</sub> (001) samples with varying LaAlO<sub>3</sub>-layer thickness  $x$ . (a) LaAlO<sub>3</sub> layers grown on the TiO<sub>2</sub>-terminated SrTiO<sub>3</sub> substrates forming  $n$ -type interfaces. The bottom panel shows difference spectra from that of SrTiO<sub>3</sub>. (b) LaAlO<sub>3</sub> layers grown on the SrO-terminated SrTiO<sub>3</sub> substrates forming  $p$ -type interfaces. (c) Ti<sup>3+</sup> intensity ratio of the Ti 2p core-level spectra as a function of  $x$ . The dashed curve is a guide to the eye.

started to increase gradually well below 4 uc. This suggests that the electronic reconstruction or charge transfer to the interfacial region occurred already below the critical thickness as reported in a previous work [24]. A similar behavior was also observed in polar multilayers LaAlO<sub>3</sub>/LaVO<sub>3</sub>/LaAlO<sub>3</sub> [25, 26], suggesting that the transport properties of interfaces, which show an abrupt change at 4 uc, are not solely determined by the carrier number but also by the carrier mobility [13], perhaps involving a percolation threshold. As the origin of the gradual electronic reconstruction, we consider surface defects and/or adsorbed molecules on the LaAlO<sub>3</sub> surface, such as oxygen vacancies which generate and donate electrons to the  $n$ -type interface. A similar mechanism has been discussed by Cen *et al.* to explain the creation of metallic regions using a conducting AFM tip [27]. This mechanism has been taken into account in the theoretical description of the LaAlO<sub>3</sub>/SrTiO<sub>3</sub> interface by Bristowe *et al.* [28]. According to their calculation, the Ti<sup>3+</sup> component gradually appears below the critical thickness and reproduces our experimental observation of Ti<sup>3+</sup> below 4 uc [Fig. 3(c)]. In fact, a recent study has shown that adsorption of polar solvents on the surface of LaAlO<sub>3</sub>/SrTiO<sub>3</sub> samples induces charge carrier at the interface, indicating remote charge transfer from the surface to the interface [29]. The difference between the amount of Ti<sup>3+</sup> determined by photoemission and the carrier density determined by the transport measurements below 4 uc indicates that all the carriers in the Ti 3d band are localized below 4 uc [29].

We have also studied the core-level shifts as functions of the LaAlO<sub>3</sub>-layer thickness as shown in Fig. 4. Figure 4(a) and (b) indicates that, with increasing LaAlO<sub>3</sub> thickness, all the core levels of LaAlO<sub>3</sub> are shifted by the same amount [Fig. 4(a)] and those of SrTiO<sub>3</sub> are also shifted by the same amount [Fig. 4(b)] (including charging effects), while the core levels of LaAlO<sub>3</sub> and those in SrTiO<sub>3</sub> are shifted to a different degree [Fig. 4(c)]. Considering the fact that the intensity of photoemission

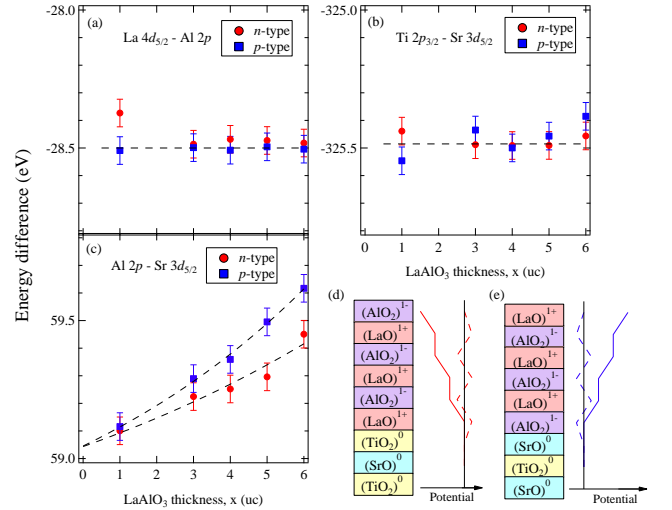


FIG. 4: (Color online) Shifts of core levels for LaAlO<sub>3</sub>( $x$  uc) thin films grown on the SrTiO<sub>3</sub> substrates. (a) Relative shifts within the LaAlO<sub>3</sub> layers. (b) Relative shifts within the SrTiO<sub>3</sub> substrates. (c) Relative shifts between the LaAlO<sub>3</sub> and SrTiO<sub>3</sub> layers. (d),(e) Schematic diagram of the Madelung potential in the LaAlO<sub>3</sub>/SrTiO<sub>3</sub> samples with the  $n$ -type and  $p$ -type interfaces. The dashed and solid curves represent the electrostatic potential with and without electronic reconstruction, respectively.

signals decreases exponentially with depth, the shifts of the La and Al core levels represent the electrostatic potential at the surface and those of Sr and Ti core levels represent the electrostatic potential at the interface. According to the polar catastrophe model, the shift should be as large as  $\sim 1$  eV/uc until the critical thickness of 4 uc is reached, where the top of the O 2p band at the LaAlO<sub>3</sub> surface is raised above the bottom of the Ti 3d band of SrTiO<sub>3</sub>. Figure 4(c) indicates that the exper-

imental core-level shifts of the  $\text{LaAlO}_3$  layer relative to those of the  $\text{SrTiO}_3$  were less than  $\sim 0.1$  eV/uc. Furthermore, the relative shifts were in the same direction for the  $n$ -type and  $p$ -type interfaces, in contrast to the expectations of the polar catastrophe model shown in Fig. 4(d) and (e). In Ref. [21], the shifts were also small but the relative shifts between the  $n$ -type and  $p$ -type interfaces were opposite to the present result. The existence of charged defects at the surface and resulting charge transfer from the surface to the interface explain the reduction of the core-level shifts from  $\sim 1$  eV/uc to  $\sim 0.1$  eV/uc, but the remaining small shifts may depend on the subtle charge distribution and may vary between the samples prepared by the MBE method [21] and the present PLD method.

In conclusion, we have performed a core-level photoemission spectroscopy study of  $\text{LaAlO}_3/\text{SrTiO}_3$  interfaces as a function of  $\text{LaAlO}_3$ -layer thickness. Only for  $\text{LaAlO}_3$  grown on  $\text{TiO}_2$ -terminated  $\text{SrTiO}_3$  substrates ( $n$ -type interface), the Ti  $2p$  core-level spectra showed a  $\text{Ti}^{3+}$  com-

ponent in addition to  $\text{Ti}^{4+}$ . The amount of the  $\text{Ti}^{3+}$  component was significantly larger than the carrier densities estimated from transport measurements, indicating that part of the carriers at the interfaces are localized. The gradual rather than abrupt appearance of the  $\text{Ti}^{3+}$  component with the growth of the  $\text{LaAlO}_3$  layer as well as the absence of the large core-level shifts expected from the polar catastrophe model suggests that the evolution of charged surface defects or adsorbates needs to be involved beyond the simplest polar catastrophe model [28].

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